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THERMODYNAMICS OF KETONES + ETHER MIXTURES USING A GENERALIZED QUASICHEMICAL THEORY IN TERMS OF GROUP SURFACE INTERACTIONS

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ABSTRACT

A general quasichemical theory in terms of group surface interactions is presented. The theory is applied to ketones (symmetrical and asymmetrical) + monoether (di-n-butyl ether). Comparison with experimental enthalpies shows quite satisfactory agreement for all of the systems investigated. Possible sources of discrepancy and ways of refining the model are discussed.

INTRODUCTION

The thermodynamic excess functions of organic liquid mixtures depend on the chemical nature, size and shape of the constituent molecules. For molecules of dissimilar molecular nature but nearly the same size and shape, the differences in forces fields produce the main contribution to the thermodynamic excess functions.

Since it is practically impossible to predict quantitatively the chemical contribution, one has to adjust a few parameters for each binary system in order to describe properties of mixtures. A significant saving of adjustable parameters can be realized for classes of organic molecules which are ensembles of distinct functional groups, when each "group" consists of a few atoms and is situated in a given intramolecular environment. A large number of compounds can be thus formed from a relatively small number of groups.

Interaction parameters are adjusted to characterize each pair of groups and the properties of binary or multicomponent mixtures may be predicted in terms of these parameters.

The purpose of this paper is to present the general theory, in the group surface version [1–5], by using a theory which is essentially identical with the Guggenheim–Barker [6] quasi-lattice theory, and to illustrate its application to binary mixtures (ketones + monoether).

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THEORY

The model used in this paper is a simple extension of Guggenheim–Barker quasi-lattice theory, called DISQUAC (dispersive-quasichemical model) [7,8].

In this model there are two contributions; quasichemical contribution and dispersive contribution. The fundamental supposition of the DISQUAC model is to obtain two interaction terms in the thermodynamics functions such as the addition of two contributions: (i) dispersive contribution ($G^{\mathrm{E,\,disp.}}_{\mathrm{int}}$, $H^{\mathrm{E,\,disp.}}$); (ii) quasichemical contribution ($G^{\mathrm{E,\,quac.}}_{\mathrm{int.}}$, $H^{\mathrm{E,\,quac.}}$)

The excess Gibbs free energy and the excess enthalpy will be

$$G^{\mathrm{E}} = G^{\mathrm{E}}_{\mathrm{comb.}} + G^{\mathrm{E,\,disp.}}_{\mathrm{int.}} + G^{\mathrm{E,\,quac.}}_{\mathrm{int.}} \tag{1}$$

$$H^{\mathrm{E}} = H^{\mathrm{E,\,disp.}} + H^{\mathrm{E,\,quac.}} \tag{2}$$

where $G^{\mathrm{E}}_{\mathrm{int.}}$ is the term of interaction and $G^{\mathrm{E}}_{\mathrm{comb.}}$ is the Flory–Huggins combinatorial

$$G^{\mathrm{E}}_{\mathrm{comb.}} = RT\sum_i x_i \ln\frac{\rho_i}{x_i} \tag{3}$$

where ρ_i is the volume fraction of component i.

The dispersive contribution for excess Gibbs free energy and the excess enthalpy at the zero approximation is [9]

$$G^{\mathrm{E,\,disp.}}_{\mathrm{int.}} = 0.5\sum_i (q_i x_i)\sum_i\sum_j \xi_i\xi_j g^{\mathrm{disp.}}_{ij} \tag{4}$$

$$H^{\mathrm{E,\,disp.}} = 0.5\sum_i (q_i x_i)\sum_i\sum_j \xi_i\xi_j h^{\mathrm{disp.}}_{ij} \tag{5}$$

where q_i is the surface of contact of molecule i, x_i is the molar fraction of component i in the mixture and ξ_i is the surface fraction of component i in the mixture and

$$g^{\mathrm{disp.}}_{\mathrm{ij}} = -0.5\sum_s\sum_t (\alpha_{si}-\alpha_{sj})(\alpha_{ti}-\alpha_{tj}) g^{\mathrm{disp.}}_{st} \tag{6}$$

$$h^{\mathrm{disp.}}_{\mathrm{ij}} = -0.5\sum_s\sum_t (\alpha_{si}-\alpha_{sj})(\alpha_{ti}-\alpha_{tj}) h^{\mathrm{disp.}}_{st} \tag{7}$$

where α_{si} is the surface fraction of type s on a molecule of type i, $g^{\mathrm{disp.}}_{st}$, $h^{\mathrm{disp.}}_{st}$ are two interchange dispersive parameters of contact (s, t).

For a binary system, the quasichemical contribution is

$$G^{\mathrm{E,\,quac.}}_{\mathrm{int}} = x_1\mu^{\mathrm{E,\,quac.}}_{\mathrm{int,\,1}} + x_2\mu^{\mathrm{E,\,quac.}}_{\mathrm{int,\,2}} \tag{8}$$

where μ^{E}_i is the excess molar chemical potential of component i

$$\mu^{\mathrm{E,\,quac.}}_{\mathrm{int,\,1}} = zq_1\sum \alpha_{si}\ \ln\frac{X_\alpha\alpha_{si}}{X_{si}\alpha_s}(i = 1, 2, \ldots) \tag{9}$$

$$H^{\mathrm{E,\,quac.}} = 0.5(q_1x_1 + q_2x_2)\sum_s\sum_t (X_sX_t - (\xi_1X_{s1}X_{t1} + \xi_2X_{s2}X_{t2}))\eta_{st}h^{\mathrm{quac}}_{st} \tag{10}$$

where

$$\eta_{st} = \exp(-g_{st}^{\text{quac.}}/zRT) \tag{11}$$

$g_{st}^{\text{quac.}}$ and $h_{st}^{\text{quac.}}$ are the interchange quasichemical parameters of contact (s, t) and z represents the number of possible orientations that can exist between two surfaces in contact. For X_s and X_t we obtain the system of λ equations (λ is the number of different surfaces, contact or functional groups)

$$X_s\left(X_s + \sum X_t\eta_{st}\right) = \alpha_s(s,\ t = a,\ b, \ldots \lambda) \tag{12}$$

This X_{si} and X_{ti} $(i = 1,\ 2)$ are the solutions of the system of eq. (12) for $x_i = 1$.

Since we use independent determinations of both g^{E} and h^{E} at different temperatures, we have assumed a temperature dependence of the Gibbs energy interchange parameter g_{st} according to the equation

$$g_{st}(T)/RT = C_{st,1} + C_{st,2}\left(\left(T^{\ominus}/T\right) - 1\right) \tag{13}$$

where $T^{\ominus}$ is a reference temperature (generally 298.15 K). The constants $C_{st,i}$ are numbers (independent of the unit chosen) which have the following significance

$$C_{st,1} = g_{st}^{\ominus}/RT^{\ominus} \tag{14}$$

$$C_{st,2} = h_{st}^{\ominus}/RT^{\ominus} \tag{15}$$

where $g_{st}^{\ominus} = g_{st}(T^{\ominus})$ and $h_{st}^{\ominus} = h_{st}$ (independent of T).

ASSESSMENT OF GEOMETRICAL PARAMETERS

In the theory developed above each type of molecule i is characterized by the following set of geometrical parameters: the total surface q_i, the molecular surface fractions α_{si} and the volume r_i. In order to account for the constitution of organic molecules realistically, we consider them as ensembles of identifiable structural units corresponding to the main chemical groups. We have here adapted the method developed by Bondi [10,11]. In this more elaborate method each atom is considered to be spherical and the volume V_{G} and the surface A_{G} of a given group G, composed of various atoms, are calculated on the basis of the geometry of bonded atoms with interpenetrating surfaces. The fraction of surface (and therefore of volume) left for a possible contact is calculated from the covalent radii and the van der Waals radii [12,13]. As volume and surface units we arbitrarily decided to take the volume and surface of methane (CH_4).

TABLE 1

Relative group increments for molecular volumes $r_G = V_G/V_{CH_4}$, and areas $q_G = A_G/A_{CH_4}$ calculated by Bondi's method. ($V_{CH_4} = 17.12\ 10^{-6} m^3 mol^{-1}$, $A_{CH_4} = 2.90\ 10^{-6} m^2 mol^{-1}$)

Group	r_G	q_G
CH_4	1.00000	1.00000
CH_3-	0.79848	0.73103
$-CH_2-$	0.59755	0.46552
-O-	0.21612	0.20690
-CO-	0.68344	0.55174

TABLE 2

Volumes r_i, total surfaces q_i, and molecular surface fractions α_{si}, calculated from the relative group increments r_G and q_G given in Table 1

	r_i	q_i	α_{ai}	α_{ei}	α_{ci}
2-Butanone	2.87790	2.47930	0.77750	0.00000	0.22250
2-Pentanone	3.47550	2.94480	0.81260	0.00000	0.18740
2-Hexanone	4.07300	3.41030	0.83820	0.00000	0.16180
2-Heptanone	4.67060	3.87590	0.85770	0.00000	0.14230
2-Octanone	5.26810	4.34140	0.87290	0.00000	0.12710
2-Nonanone	5.86570	4.80690	0.88520	0.00000	0.11480
3-Pentanone	3.47550	2.94480	0.81260	0.00000	0.18740
4-Heptanone	4.67060	3.87590	0.85770	0.00000	0.14230
5-Nonanone	5.86570	4.80690	0.88520	0.00000	0.11480
Di-n-butyl ether	5.39838	4.46208	0.95363	0.04637	0.00000

α_{ai}, aliphatic chain; α_{ei}, oxygen group; α_{ci}, carbonyl group.

The geometrical parameters, i.e. the relative group increments r_G and q_G, concerned in this study are given in Table 1. The volume r_i, the total surface q_i, and the areas q_{si} were calculated additively using the corresponding group increments. The molecular surface fractions were calculated as defined by the equation $\alpha_{si} = q_{si}/q_i$. The values of r_i, q_i and α_{si} of all molecules investigated in this paper are given in Table 2.

ESTIMATION OF INTERACTION PARAMETERS

For each binary mixture, the thermodynamic properties must be studied in a systematic way with respect to the interactions of a given functional group. Each individual pair of groups (st) is characterized by the two interaction parameters g_{st} and h_{st} and we establish a catalog of their values. To this end, we have adjusted first g_{st} and then h_{st} for each class to fit eqns. (1) and (2) to the best available experimental data for G^E and H^E respec-

TABLE 3
Interchange parameters (aliphatic–oxygen groups)

$g_{ae}^{\mathrm{dis}}/RT^{\ominus}$	$g_{ae}^{\mathrm{quac.}}/RT^{\ominus}$	$h_{ae}^{\mathrm{dis.}}/RT^{\ominus}$	$h_{ae}^{\mathrm{quac.}}/R^{\mathrm{T}\ominus}$
15.51	0.00	18.36	0.00

tively. During this procedure only one pair of parameters g_{st} and h_{st} was adjusted at a time since the key systems used contained only two types of surfaces.

Throughout this study the different types of contact surfaces have been labelled with small letters:

Contact (a,e), aliphatic (CH_3– or –CH_2–), oxygen (–O–)
Contact (a,c), aliphatic (CH_3– or –CH_2–), carbonyl (–CO–)
Contact (e,c), oxygen (–O–), carbonyl (–CO–)

In the mixtures of ketones + monoether (di-n-butyl ether) we determined all the interaction parameters reported in the study. First we considered mixtures of n-alkanes + ether: we have fitted the parameters g_{ae} and h_{ae}, respectively, with the experimental data for G^{E} and H^{E}. This study has already been carried out [14], using $z = \infty$ (random mixing) considering a dispersive contribution (Table 3).

After considering mixtures of n-alkanes + ketones and with the experimental data for G^{E} and H^{E} we have fitted the parameters g_{ac} and h_{ac}. As before, this system has been studied by H.V. Kehiaian [1,2] and he has considered a quasichemical contribution ($z = 10$, Table 4).

We can now determine the mixture of ketones + ether. For the fitting of g_{ce} we have used the experimental data for G^{E} of Abbott et al. [15] (2-propanone + diethyl ether). We have fitted the parameter h_{ce} about the experimental data for H^{E} of the system 2-butanone + di-n-butyl ether [16]. We have considered a dispersive contribution $z = \infty$ (Table 5).

TABLE 4
Interchange parameters (Aliphatic–carbonyl groups($z = 10$))

	$g_{ac}^{\mathrm{dis.}}/RT^{\ominus}$	$g_{ac}^{\mathrm{quac.}}/RT^{\ominus}$	$h_{ac}^{\mathrm{dis.}}/RT^{\ominus}$	$h_{ac}^{\mathrm{quac.}}/RT^{\ominus}$
2-Butanone	0.000	8.097	0.000	9.990
2-Pentanone	0.000	8.097	0.000	9.830
2-Hexanone	0.000	8.097	0.000	9.830
2-Heptanone	0.000	8.097	0.000	9.830
2-Octanone	0.000	8.097	0.000	9.830
2-Nonanone	0.000	8.097	0.000	9.830
3-Pentanone	0.000	7.680	0.000	9.319
4-Heptanone	0.000	7.680	0.000	8.999
5-Nonanone	0.000	7.680	0.000	8.999

COMPARISON WITH EXPERIMENT AND ANALYSIS

In this section we compare the experimental data for G^E and H^E with those calculated from eqns. (1) and (2) using the geometrical parameters listes in Tables 1 and 2 and interchange energy parameters listed in Tables 3–5. The comparison was carried out for asymmetrical and symmetrical ketones + monoether (Figs. 1 and 2). There is good agreement on the

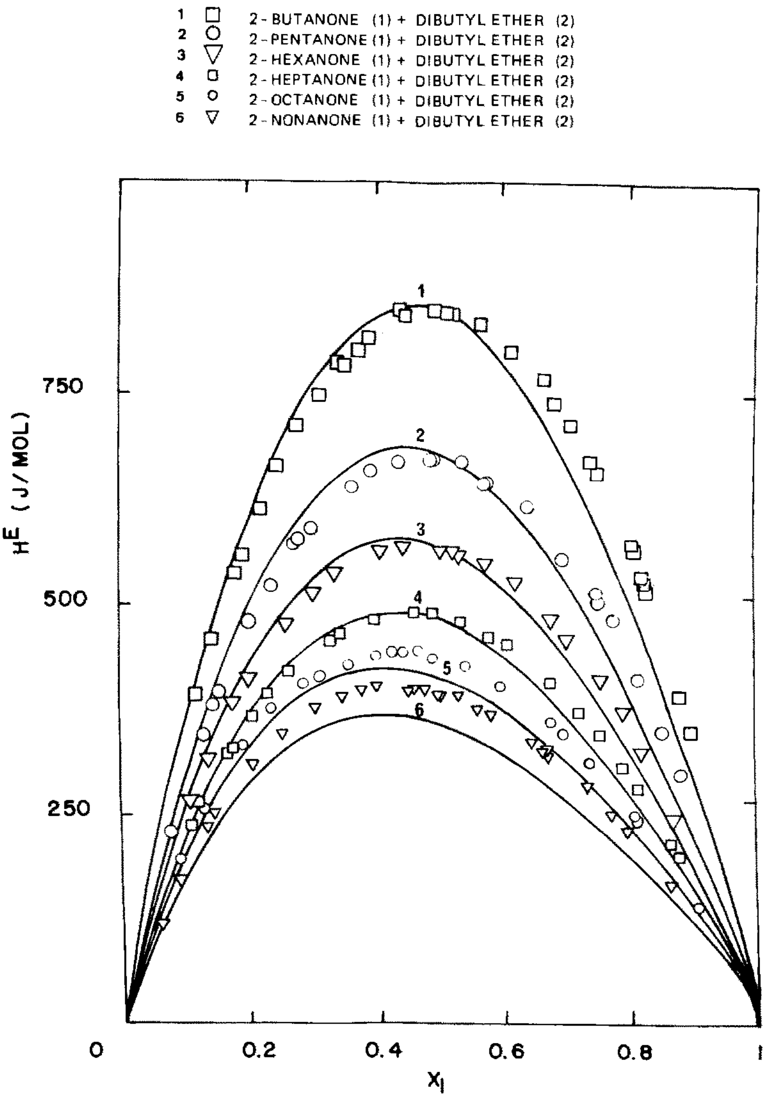

Fig. 1. Comparison of theory with experiment for the excess enthalpies, H^E of asymmetrical ketones (1) + di-n-butyl ether (2) mixtures. Full lines, predicted values; points, experimental results: data of F.J. Rey and co-workers [16].

TABLE 5
Interchange parameters (Carbonyl–oxygen groups)

$g_{ce}^{\text{dis.}}/RT^{\ominus}$	$g_{ce}^{\text{quac.}}/RT^{\ominus}$	$h_{ce}^{\text{dis.}}/RT^{\ominus}$	$h_{ce}^{\text{quac.}}/RT^{\ominus}$
1.320	0.000	−3.320	0.000

deviation of H^E with the chain length of the ketone in mixtures with monoether.

The analysis of the experimental results presented in this paper (Figs. 1 and 2) demonstrates the usefulness of our simple group contribution theory

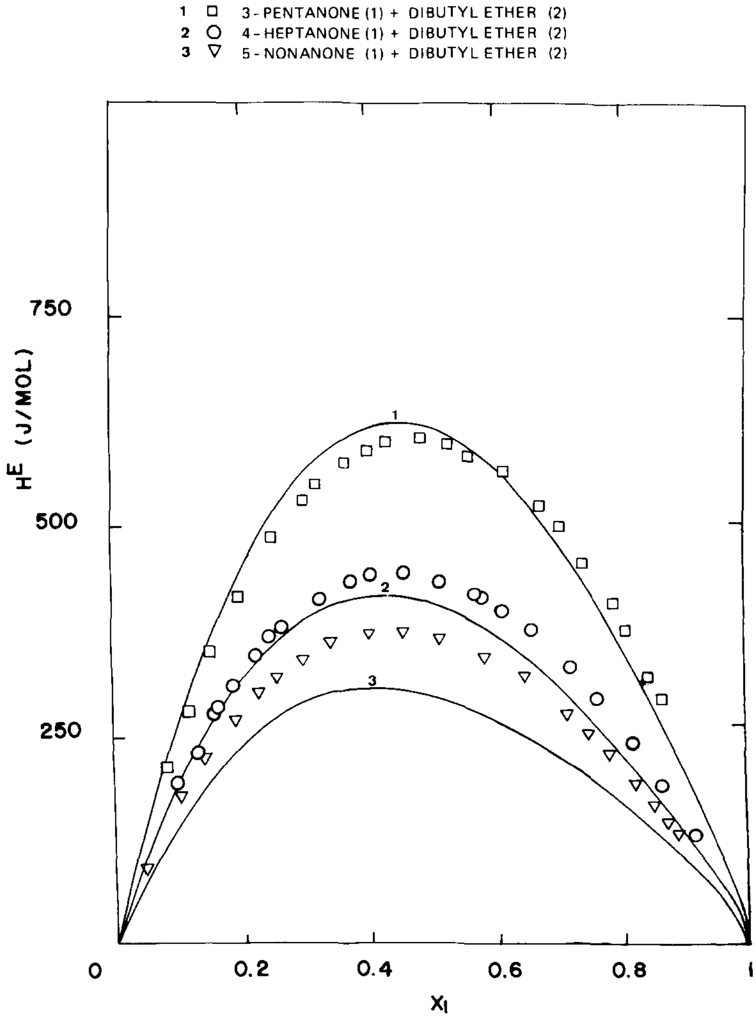

Fig. 2. Comparison of theory with experiment for the excess enthalpies, H^E of symmetrical ketones (1) + di-n-butyl ether (2) mixtures. Full lines, predicted values; points, experimental results: data of F.J. Rey and co-workers [16].

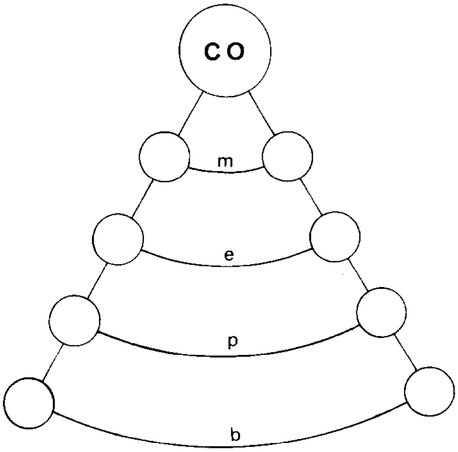

Fig. 3. Number of carbon atoms in the different levels around groups (–CO–). m, e, p, b are (CH_3–), (CH_3–CH_2–), (CH_3–CH_2–CH_2–) and (CH_3–CH_2–CH_2–CH_2–) respectively.

for predicting the excess enthalpies of our systems. However for the mixtures of longer chain lengths compounds (di-n-butyl ether + 2-octanone, 2-nonanone, 4-heptanone and 5-nonanone) the theory shows a negative deviation with respect to the experimental data. This characteristic is similar to that of other type of systems [17–20].

This effect is supposed to be of “steric” type. The model used by us does not describe it but, as in other studies [17–20], we have supposed that the interchange energy parameters are a function of the increment of the alkyl group $\sigma^R_{ce,2}$ given by the equation

$$C^R_{ce,2} = C^{\ominus}_{ce,2}\left(1 + n^e\sigma_{ce,2} + n^e\sigma_{ce,2} + n^p\sigma_{ce,2} + n^b\sigma_{ce,2} + \dots\right) \tag{16}$$

where $C^{\ominus}_{ce,2}$ is the interchange parameter of the component base (2-propanone), n^e, $n^p, \dots$ are the number of carbon atoms in the different level around the group (–CO–), and e, p, b, are (CH_3–CH_2–), (CH_3–CH_2–CH_2–) and (CH_3–CH_2–CH_2–CH_2–), respectively (Fig. 3.)

This procedure was used to recalculate the interchange parameter $h^{\text{dis}}_{ce}/RT^{\ominus}$. After fitting the parameter σ^R_{ce} in eqn. (16) as a standard method of linear multiple regression, the parameter h^{dis}_{ce} was found to fit better for each system investigated. The values of the parameter σ^R_{ce} are shown in Table 6.

Since to get the parameter σ^R_{ce} we have calculated eqn. (16), the new values of interchange parameters $h^{\text{dis}}_{ce}/RT^{\ominus}$ for all systems investigated are shown in Table 7.

TABLE 6

Parameters of the incremental alkyl group from eqn. (16)

$h^{\ominus,\text{dis.}}_{ce}/RT = C^{\ominus}_{ce,2}$	σ^e_{ce}	σ^p_{ce}	σ^b_{ce}
−6.183	−0.222	−0.200	−0.102

TABLE 7
Interchange parameters (carbonyl–ether groups)

	$h_{ce}^{\text{dis.}}/RT^{\ominus}$	$h_{ce}^{\text{quac.}}/RT^{\ominus}$
2-Butanone	−4.81	0.00
2-Pentanone	−3.58	0.00
2-Hexanone	−2.94	0.00
2-Heptanone	−2.31	0.00
2-Octanone	−1.68	0.00
2-Nonanone	−1.05	0.00
3-Pentanone	−3.44	0.00
4-Heptanone	−0.97	0.00
5-Nonanone	0.30	0.00

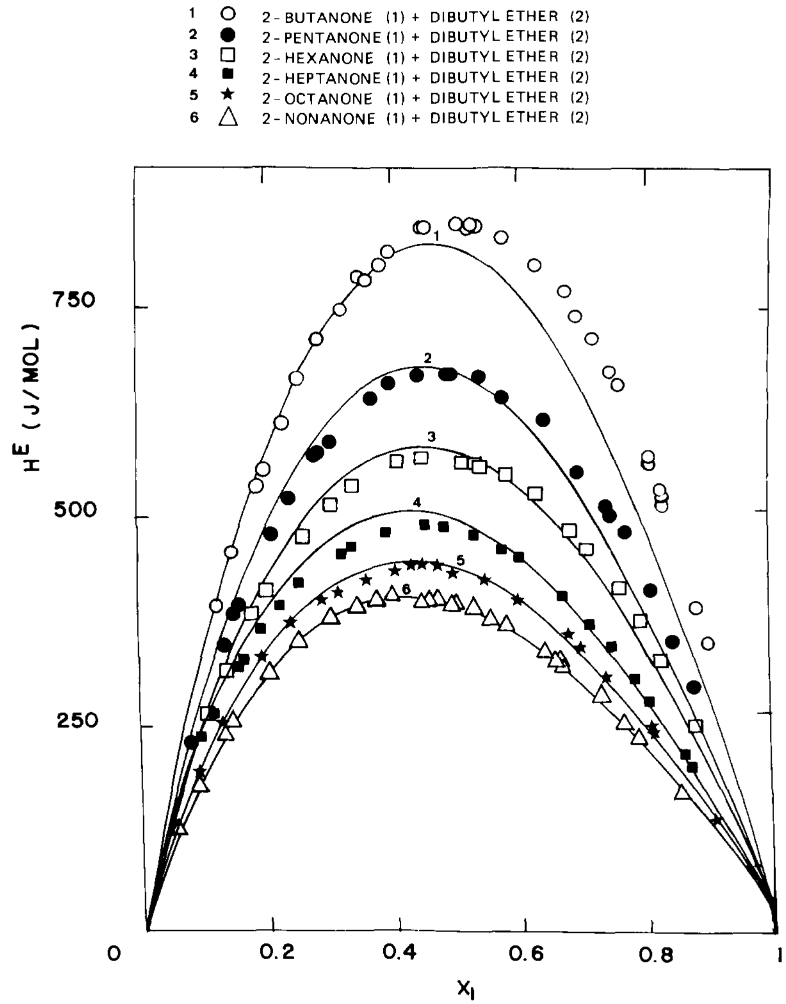

Fig. 4. Comparison of theory (we assume an effect of a "steric" type, using the new parameters of Table 7) with experiment for the excess enthalpies, H^E of asymmetrical ketones (1) + di-butyl ether (2) mixtures. Full lines, predicted values; points, experimental results: data of F.J. Rey and co-workers [16]. The agreement is better than in Fig. 1.

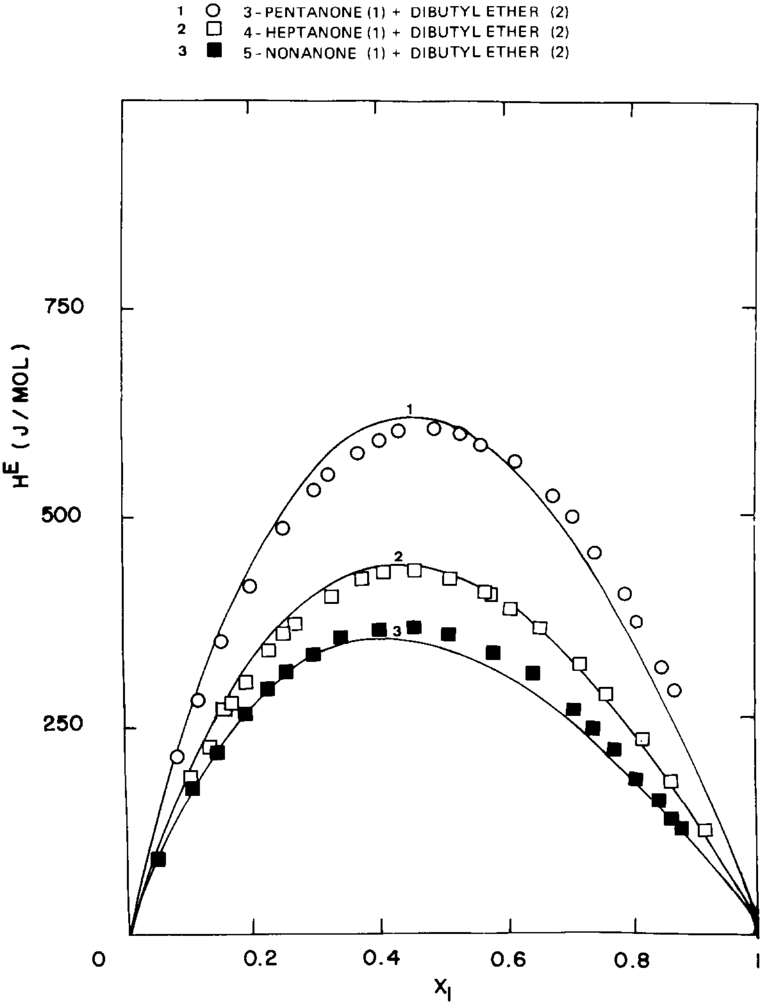

Fig. 5. Comparison of theory, (we assume an effect of a "steric" type, using the new parameters of Table 7) with experiment for the excess enthalpies, H^E of symmetrical ketones (1)+di-n-butyl ether (2) mixtures. Full lines, predicted values; points, experimental results: data of F.J. Rey and co-workers [16]. The agreement is better than in Fig. 2.

Using the parameters of Table 7, we have compared theoretical and experimental excess enthalpies for binary mixtures of ketones + di-n-butyl ether.

The agreement is satisfactory as already shown in Figs. 4 and 5.

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